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JULY 1962

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METALLIC SURFACES N64 10372 *

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DOUGLAS V. KELLER, JR.

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METALLIC SURFACES**

Prepared for:

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND**

Submitted by

Douglas V. Keller, Jr.

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SYRACUSE UNIVERSITY RESEARCH INSTITUTE

DEPARTMENT OF CHEMICAL ENGINEERING AND METALLURGY

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PART I
BULK ADHESION

ADHESION BETWEEN ATOMICALLY CLEAN METALLIC SURFACES*

by

T. Spalvins
D.V. Keller.

* Text Presented: American Vacuum Society, Metallurgy Division Conference, New York University, June 18, 19, 1962 and will be published in the proceeding of the Symposium. The basis of this publication was presented as a Master's Degree Thesis by T. Spalvins.

ADHESION BETWEEN ATOMICALLY CLEAN METALLIC SURFACES

Introduction

The results of two metals coming into contact with each other have received considerable research attention under the various headings of friction, pressure welding, sintering, fretting corrosion, electrical contact phenomena, and the like. Although the mechanisms of these processes appear to be independent on a macroscale; there is considerable evidence that the atomic scale mechanisms are quite similar. That is, in all cases the metallic substrate atoms of each surface must be brought into intimate contact before adhesion takes place (1). For example, this study was inaugurated as an outgrowth of a friction research program. There seems to be little doubt at this time that the general friction mechanism proposed by Bowden's Group in England which involves the basic components of a) Mechanical "Plowing" Action, and b) The Shearing of "Microwelds", is well established and widely accepted. The "plowing" component is the result of two surface asperities, or irregularities, scraping over each other during sliding while the welding component occurs as the result of metallic atoms of one surface actually bonding to the atoms of the second surface. The mechanism of formation of these microwelds as a function of composition, structure and temperature has received little attention until recently since the microwelding component could be reduced to a minimum through the use of lubricants which prevented intimate contact of the surfaces. However, in high or ultra-high vacuum applications, most lubricants lose their effectiveness or tend to evaporate and the seizure problem is increased manyfold. This problem in itself justified a closer look at the mechanism of metallic adhesion. The adhesion

of one metal to another was observed by several investigators as early as 1912 (2) and studied by Bowden (3) in 1936. The study consisted of rubbing one metal on a plate of similar material and observing the effect of surface impurities on the degree of seizure. Nickel couples and platinum couples formed seizure welds in evacuated systems. Since this time, Bowden's Group and many other groups have reported results of vibrators, impactors, or sliders operating upon a plate in which the slider, or indenter, and plate were fabricated from various combinations of materials and the apparatus exposed to different atmospheres and vacuum to 10^{-6} Torr (mm Hg). The conclusions suggested that the degree of seizure was a function of couple composition, atmosphere, mechanical properties, force, speed of movement and surface contamination. In most cases, however, the mechanics of the contact area appeared to be most important, rather than the surface chemistry of the adhesion components.

A second approach to the problem was suggested recently by Rabinowicz (4) in the form:

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab}$$

Where: W_{ab} = Work of Adhesion

γ_i = Free surface energy

γ_{ab} = Interfacial free energy

which is similar to the equation suggested by Harkins in 1917 (5) for surface wetting of solids. The equation as applied to simple solid adhesion, however, appears to be somewhat oversimplified as will be illustrated later.

In order to shed a little more light on some of the problems just outlined,

an experiment was designed to bring two clean metallic surfaces into touch contact at a near zero force and determine whether or not adhesion welding took place. According to Farnsworth (6), Hagstrum (7) and other researchers (8) on the preparation of atomically clean metallic surfaces, a pure surface can be prepared with a relatively high degree of certainty, if the following conditions are met:

- a) Degassing of metallic sample at high temperatures and low pressures,
- b) Removal of impure surface layers.
- c) Prevention of reformation of impure surface layers by gas adsorption.

The first condition was satisfied by a prolonged anneal of the metallic components in a system at a temperature just below the fusion point and a pressure of at least 10^{-6} Torr or by the use of vacuum melted materials. The second requirement was implemented in our experiments by removal of the surface layers within a ultra high vacuum system by the use of argon ion bombardment with a subsequent removal of the adsorbed argon. Readsorption of the gaseous elements was prevented through the period of the experiment by operation at pressures in the range of 10^{-11} Torr as demonstrated by Redhead (9).

Experimental

The Apparatus designed for this study is shown in Figure I. The 1 x 2 cm sample plate (A) and 0.3 cm (O.D.) indenter (B) were supported on pyrex insulator tubes which were in turn mounted on vac melted iron slugs (D). The iron slugs could be moved $\pm 3/4$ " by a magnet or solenoid.

The UHV system (2×10^{-11} Torr) was separated from the LV system (1×10^{-7} Torr) by a Granville-Phillips valve (H). The LV system was used to evacuate the UHV cell during the 450°C , 8 hour bake-out cycle and to move the high purity argon gas from the getter flask (K) into the cell for ion bombardment. The LV system consisted of a Duo-Seal mechanical pump and a two stage Hg diffusion pump isolated from the UHV cell by two large volume, liquid nitrogen traps (I). The pressure within this system was measured by a CVC discharge gauge (GPH -100 g) (J).

Tank argon was gettered by evaporating about 200 mg of pure barium* at a pressure of 10^{-6} Torr on the walls of a thoroughly degassed 500 ml flask attached to the low vacuum system through a three-way stopcock. The flask was then flooded with tank argon and allowed to stand over a period of hours, while the impurities, water vapor, oxygen, nitrogen and etc. reacted chemically with the barium.

Upon completion of bake-out cycle and the degassing of the filaments (C and G) the G-P valve was closed and titanium was evaporated (G) until the pressure within the cell was about 2×10^{-11} Torr as measured with the inverted magnetron gauge (NRC -552, 752) (F). The titanium was evaporated from a tungsten helix in short bursts such that the pyrex container remained cool; thus, preventing back diffusion of the adsorbed gases. About five flashes were required to obtain the desired working pressure. Pure argon was then admitted to the cell from the getter ballon to a pressure of about 10^{-3} Torr; and, a potential of about 4kv was placed between the indenter and sample plate. Power from the outside to the components was achieved by glass to metal through seals. Ionic bombardment was continued and the polarity revised until both surfaces were bril-

* King Laboratories Inc., Syracuse 3, New York

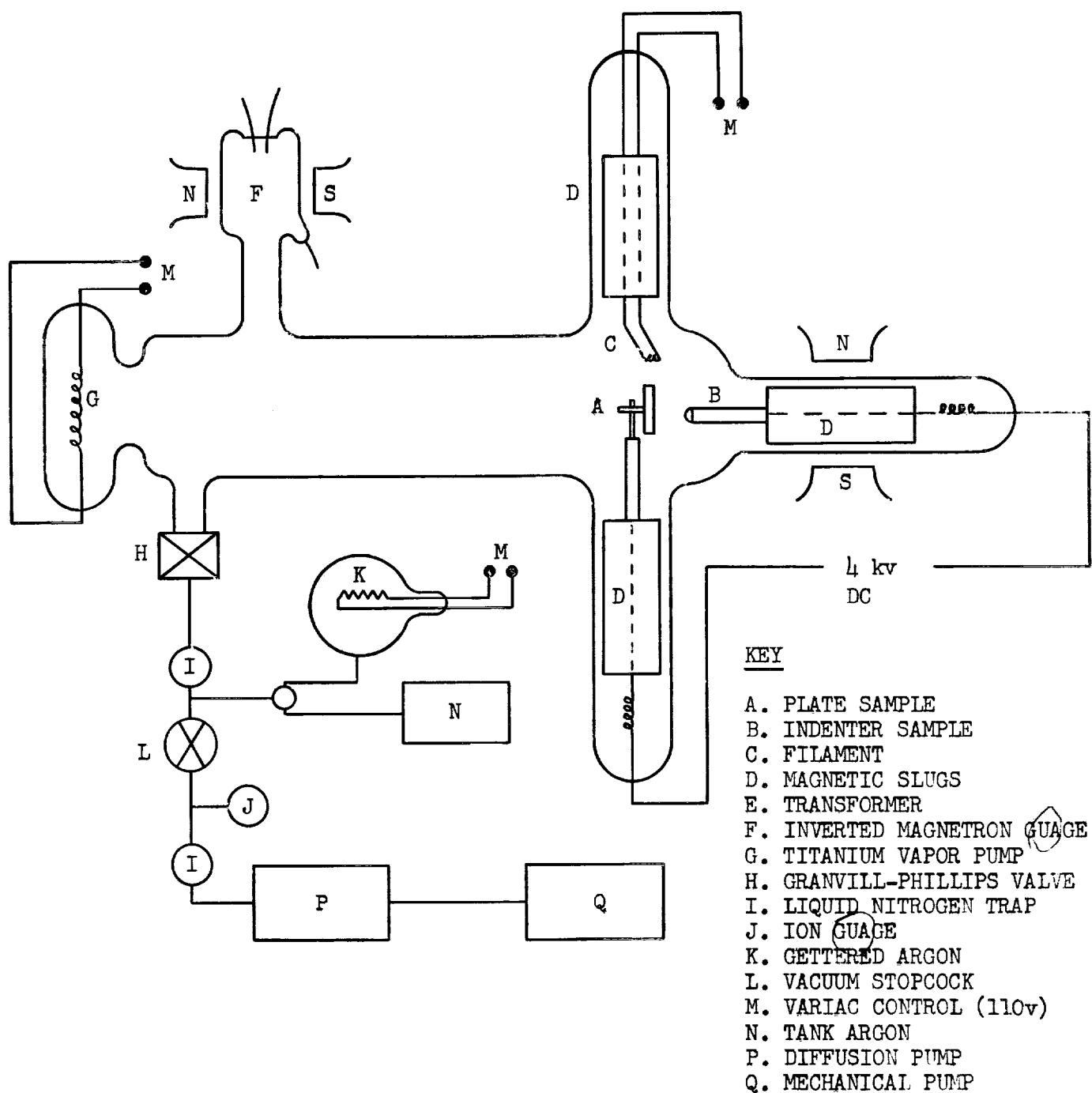


FIGURE 1 ADHESION APPARATUS

liant in appearance. The amount of surface material removed was indicated by the amount of sputtered material that condensed on the cell wall.

With the completion of ion bombardment the cell was reevacuated and given a short bake-out cycle. Upon cooling a potential was placed between the tungsten filament (C) and the test samples and several short bursts of electron bombardment were used to strip the adsorbed argon from the test surfaces. When the samples had cooled and the pressure returned to 2×10^{-11} Torr, the indenter was moved into near weightless contact with the plate by the manipulation of a magnet. The initial force of contact was calibrated before hand in an open system with a standard indenter (contact point radius of curvature about 0.32 cm) to a value of 5 grams or less. This force should be well within the bulk elastic range of the metals studied, but would exceed the elastic limit of surface asperities.

Adhesion was measured as the force on a strain guage as the indenter was removed from touch contact with the plates and later by careful metallographic inspection of the contact area. When adhesion did occur, the indenter welded to the plate and a considerable force was required for its removal. Visual and metallographic inspection of the weld area left little doubt that a complete adhesion weld did occur. When no adhesion occurred, the surfaces of the plate and indenter were undisturbed as evidenced by careful metallographic inspection at magnifications of 1000 x.

The results of tests on 8 couples in which a test consisted of at least two complete separate runs are as follows:

9 listed

Complete Adhesion

Fe - Al

Ag - Cu

Ni - Cu

Ni - Mo

No Adhesion

Cu - Mo

Ag - Mo

Ag - Fe

Ag - Ni

Ge - Ge (single crystal)

Discussion of Results

Though the results of this study cannot be approached at a mathematical level they do suggest an adhesion mechanism which depends upon the physical chemistry of the surfaces rather than the mechanical aspects of the contact area. This appears to be in better agreement with the known properties of surfaces.

Since Harkin's Equation relates to the liquid state where atomic structure may presumably be disregarded the application of the work of adhesion equation to the solid state adhesion problem appears to be an over simplification. For Example, if we substitute one half of the cohesive energy for the surface energy in this equation as a crude first approximation as suggested by Adamson (10), and then determine the work of adhesion (W_{ab}) between two pure (111) planes of germanium which are oriented to coincide on an atomic scale, we would obtain a zero work of adhesion. The result of such an occurrence, however, should be equivalent to the cohesive energy of the germanium.

When two different metals constitute the contacting surface, ie. metal A and metal B, during adhesion, the system at the interface should be considered non-equilibrium, since at room temperature relatively little bulk diffusion

should occur. Thus an ideal interface would consist of a plane separating pure A atoms and pure B atoms. Since it is unlikely that the lattice size and / or structure of A and B will be identical, the strength of the bond at the interface will not only depend upon the energy of A - B atomic bond, but also on the degree of directionality inherent in this bond with respect to the parent lattice and the normal number of nearest neighbors. If this is assumed correct, then one would predict that strongly covalent bound materials, generally requiring exact bond lengths and angles with less than 6 nearest neighbors, should not respond to adhesion since precise crystallographic alignment at the interface would be almost impossible to attain. The single crystal germanium plate and indenter oriented very nearly to the (100) directions parallel to the contact directions showed no evidence of adhesion. Also in agreement is the resistance of most covalently bound materials to powder compacting below the atom diffusion temperature range.

The metallic bond, on the other hand, with 8 or more nearest neighbors appears to be quite capable of large deviations from the equilibrium position without rupture, as exemplified by the high ductility of a metal in the pure state and the retention of ductility in solid solutions. This suggests that the directionality requirements imposed on the atomic bonds in pure metals and solid solutions are not as rigid as those of the covalent type such that a nearest neighbor may be located some distance from its equilibrium position and still retain a fraction of its equilibrium bond energy. This argument is in agreement with observations of Averback (11) and electron theories of metals.

h

The energy of adhesion must therefore be a function of the loss of the free surface energy of both free surfaces which in turn is a function of their crystallographic orientation, a function of the neighbor orientation across the interface, and a function of the nature and energy of the atomic bond between species A and species B. In the case where metal A and metal B form a continuous series of solid solutions there appears to be little demand for nearest neighbor order (11); therefore, one would expect the free energy of solution A into B to add to the loss in free surface energy of both surfaces when adhesion occurs. The result should be a weld which would be strengthened with the increase of diffusion of atoms across the boundary, i.e. temperature increase. This case also serves to illustrate another weakness of the application of Harkin's work of adhesion equation to this system since an equilibrium interfacial free energy would be difficult to usualize when A and B form a continuous series of solid solutions. In contrast to this, one may consider totally immiscible phases; That is, metal A has a positive free energy of solution in B. If this positive free energy exceeds the loss in surface free energy realized by the free surfaces in interfacial formation, one would not expect bonding across the interface. Again, interfacial equilibrium is not achieved, or even initiated.

Since the behavior of metal A atoms in proximity to metal B atoms is most readily depicted by a phase diagram, these were used to establish a ^{choice} choice the couples selected for investigation.

The couples: Fe / Al, Cu / AG, Ni / Cu, Ni / Mo, all form some sort of intermediate phase denoting a negative free energy of bond formation and subsequent adhesion as observed.

The couples: Cu / Mo, Ag / Mo, Ag / Fe, Ag / Ni, all form immiscible mixtures with no adhesion observed.

In conclusion, if we apply this model to the friction problem, particularly in ultra high vacuum environments, total seizure, welding, should not result if a proper selection of mating components is made, immiscible pairs. The pure metal substrate under any conditions will probably be exposed through the "plowing" action and the pure exposed metal, in a state of high reactivity will bond to any available compatible atom. In sliding friction the compatible atom may take the form of atmospheric gas atoms, surface scale or another metal. The model also appears to be in agreement with observations of grain boundary strengths, ie. large angle grain boundaries of solid solution systems retain a large portion, if not all of the bulk strength of the system. On the other hand as an ionic or covalent type intermediate phase is approached the large angle boundaries become weaker, reaching a very brittle state at the pure intermetallic compound, ie. NiAl or Mg_2Sn .

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Comments:

I. A determination of the minimum bake-out cycle of the vacuum system described in the previous section was obtained. The UHV cell was evacuated to about 10^{-5} Torr with the Granville - Phillips valve (H) open for bake-out times and temperatures indicated in Table 1. The G.P. valve was then closed, the cell allowed to cool and the titanium getter evaporated until a minimum final pressure was attained. The UHV cell contained the component parts mentioned in the Figure 1. The pressure was measured with the inverted magnetron gauge (F).

TABLE 1

Bake-out Temperature °C	Time Hours	Minimum Pressure Torr
100	6	2×10^{-5}
220	10	8.5×10^{-9}
300	16	1.4×10^{-9}
None*	20	2×10^{-10}
450 (Normal)	16	2×10^{-11}
* The 300°C test was allowed to stand with freshly evaporated titanium another 20 hours. The excessive gas was finally adsorbed as indicated by the lower pressure.		

As is evident from Table 1 the titanium getter assembly is a very low capacity unit capable of extremely low pressures; but unable to handle

large quantities of gas. Since the system is static and the conductance of the system is extremely high, the precision of the pressure measurements is limited by the accuracy of the measuring equipment rather than the system design.

II. A 1 x 2 x 3 cm plate of Teflon was placed in the system to estimate the lowest pressure attainable with the pressure of an organic material. Without a bake-out the lowest pressure attainable by the techniques described in the previous section was 4×10^{-5} Torr. With a five hour 200°C bake-out a pressure of only 5×10^{-7} Torr was achieved. Further heating was not recommended due to possible contamination of the vacuum cell.

PART II

DETERMINATION OF THE SURFACE ENERGY OF SILVER
AT -187°C

GRADUATE ASSISTANT:

W. Franklin (Ph.D. Candidate)

DETERMINATION OF THE SURFACE ENERGY OF SILVER AT -187°C

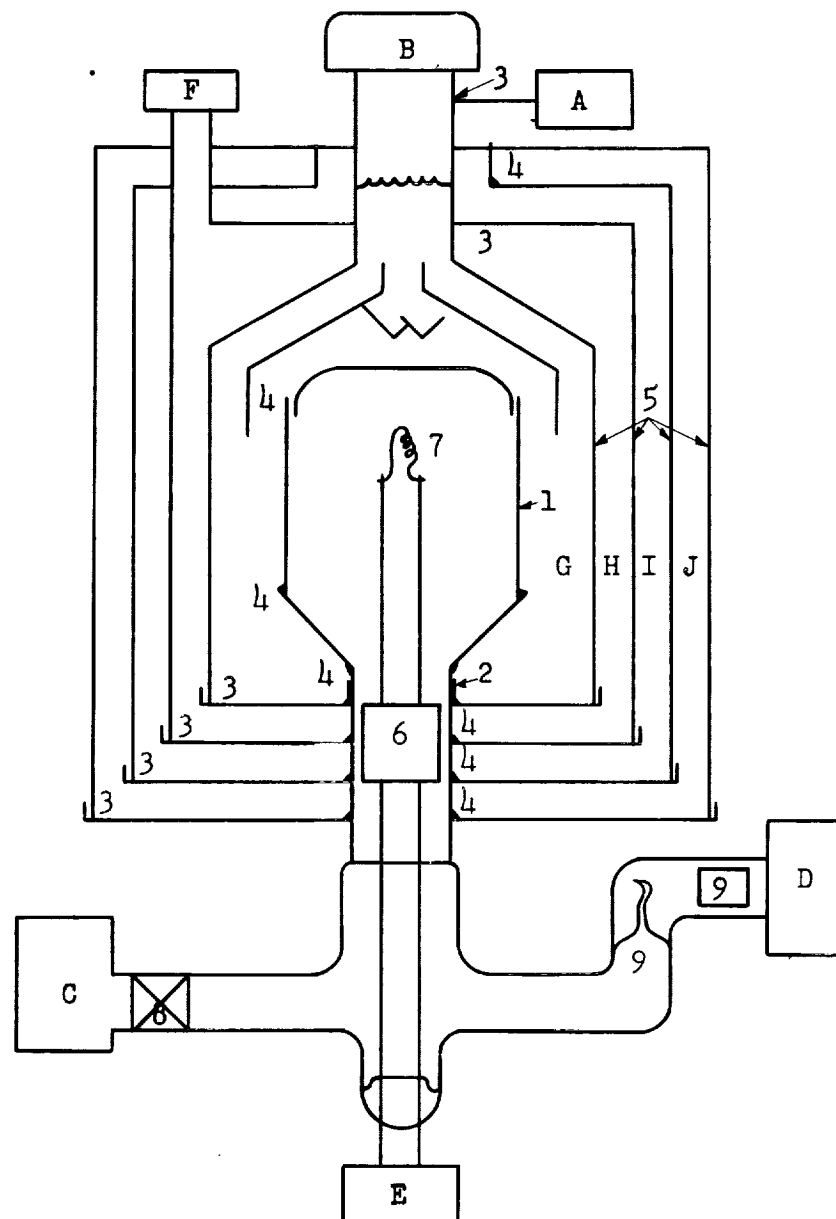
Introduction

An accurate analysis of adhesion forces requires a reasonable knowledge of the values of the surface energies of the pure free surfaces participating in the adhesion as cited in Part I of this report. The lack of these data is apparent from the literature review submitted to NASA last year (1). Briefly, techniques for the determination of solid surface energies of metals have been developed only for temperatures within a few degrees of their respective mel- melting point. The investigations rarely establish a standard surface; and, as a consequence, the scatter of data is quite large. The temperature dependence of solid surface tension is again limited to the atomic diffusional range.

In order to establish accurate low temperature values of surface energy a calorimetric technique (2) was presumed to be the direct approach. The technique will involve the change in surface area of a 0.05 g of high purity silver wire to at least 10^5 cm^2 by vaporizing the wire in a calorimeter. In order to eliminate the heats of adsorption of gases on the newly formed surface, the operation will take place at pressures below 10^{-9} Torr. For example, an adsorbed monolayer of gas on a 40 m^2 surface corresponds to about 10^{19} gas molecules while at 10^{-9} Torr only 10^{+11} molecules / liter are present which indicates that only about 10^{-6} of a monolayer can form. The container for vaporization will be silver to eliminate the heat of adhesion of the condensed silver to the walls. The electrical energy to the filament for vaporization, less the heat of condensation as observed in the calorimeter, should yield the energy

necessary for surface formation. The surface area will then be measured by BET adsorption curves using CH_4 as an adsorbant.

According to Allen et al (3) the surface area resulting from the vaporization of copper to a substrate of glass was an inverse function of the substrate temperature with -187°C providing a film of porous structure with an area of about $39.6 \text{ meters}^2 \text{ gm}^{-1}$. Since a maximum change in area will provide a maximum energy differential, a liquid argon (or nitrogen) calorimeter was designed as illustrated in Figure I. A second advantage provided in the use of a liquid gas calorimeter lies in the fact that about 14.5 cc of gas, STP, is evolved per calorie of heat input at the gas boiling point. Since the evolved volume can be measured with an accuracy of at least ± 0.5 cc, the overall accuracy of the system should be about ± 0.05 calories which is well within the limits necessary for the proposed study. The apparatus, Figure I, consists of a vaporization cell (1) attached through a Granville-Philips valve (8) to an ultra high vacuum (UHV) system (C) which is described adequately in Part I of this report and through a break-off tip (9) to the BET gas metering system for surface area determination (D). During the energy determination the BET system is isolated and during the surface area determination the UHV system (C) will be isolated. The calorimeter consists of the vaporization cell immersed in an argon bath (G) held at the boiling point by a resistance heater-thermometer. Heat exchange with the atmosphere is reduced to a minimum by concentric containers of holding vacuum (H), liquid argon (I) and polystyrene insulation (J). The super structure of the calorimeter was designed for simple disassembly to facilitate a 450°C bake-out cycle of the entire UHV system prior to silver evaporation. When the pressure within the vaporizing cell has been established



KEY

- A. CONTROLLED LIQUID ARGON SOURCE
- B. GAS BURETTE, FIG. 3
- C. UHV SYSTEM, SECTION I
- D. SURFACE AREA MEASUREMENT
- E. POWER SOURCE, FIG. 2
- F. VACUUM SYSTEM
- G. LIQUID ARGON
- H. VACUUM
- I. LIQUID ARGON
- J. INSULATION
- 1. SILVER PLATED COPPER CALORIMETER
- 2. KOVAR SEAL
- 3. REMOVABLE SOFT SOLDER JOINTS
- 4. HIGH TEMPERATURE SOLDERS
- 5. MONEL SHEET
- 6. HEAT SINK
- 7. TUNGSTEN FILAMENT
- 8. GRANVILLE - PHILLIPS VALVE
- 9. IRON SLUG AND BREAK-OFF TIP

FIGURE 1 LIQUID ARGON CALORIMETER

at about 10^{-10} Torr, the timer circuit to flash the tungsten filament from a 12 volt battery will be activated. The energy to the filament will be measured as discussed later. The heat emitted as silver vapor and radiant energy from the short flash ($\sim 1800^\circ\text{C}$) will evaporate liquid argon which will leave the liquid argon chamber at the top and pass through a small furnace at atmospheric pressure to adjust the gas temperature to 25°C . The gas will be collected over mercury in a gas burette for final pressure temperature and volume measurements. The calibrated heat leak in the calorimeter prior to flashing may be used to adjust the final observed values for total heat reaching the vaporization cell walls. Upon completion of the vaporization and energy measurements, the UHV system will be isolated and small known quantities of CH_4 will be admitted and the resulting pressures and temperatures recorded for the surface area measurements. These data will be interpreted on modified BET diagrams (4) with an accuracy of about $\pm 1\%$.

The estimated energy differential for the evaporation of 0.05 gm. silver was about 0.54 cal. from a total heat evolution of about 75 cal. as based on the following handbook values.

<u>Silver</u>	
Surface Tension	1235 dynes/cm ² (minimum value)
Heat of Sublimation	610 cal/gm (25°C)
Radiation Loss	65 cal
Surface Change	10^5 cm ²

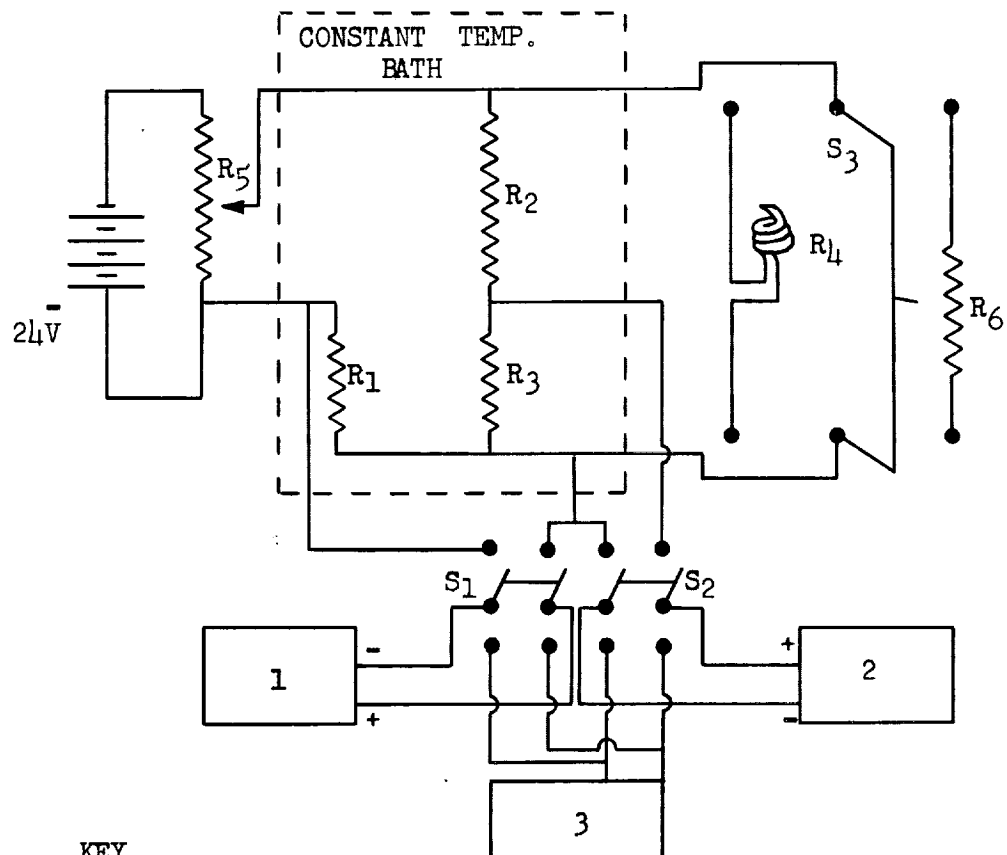
Provided a total error of about 0.1% is maintained in the energy measurement, the total error in the surface energy of about 10% should be expected. Since

no values of solid surface energy exist at or below room temperature and the values assumed above are set for maximum error, the approach appears to be justified.

Experimental

The design of the calorimeter and component parts, shown in Figure 1, was such that the vaporization chamber (1), break-off tip (9), and the ultra-high vacuum unit (C) could all be subjected to the usual 450°C bake-out. This was accomplished by removing the sheet monel super structure at the soft solder points marked (3). The monel support plates (0.062 in.) at the bottom are silver soldered (4) to the 3/4" kovar glass-metal seal (2) and the 3 x 5 x 0.010 in. silver soldered, silver-plated copper calorimeter (1) are permanent installations which readily fit into the bake-out chamber. Heat leak in the form of vaporized argon from (G) into the gas burette prior to the flashing of the silver from the tungsten coil (7) is reduced by a series of insulators and is measured carefully such that the final gas volume after the silver vaporization may be adjusted for the heat leak rate during the run period. The power to the 0.004" tungsten vaporizing coil is supplied from a twenty-four volt battery with a power control (R_5) as shown in Figure 2.

The power is passed through a dummy load (R_6) for adjustment of the two high speed Brown Recorders (1, 2) and stabilization of the source prior to vaporizing the silver. To vaporize the silver a precision timer is excited for a given time which switches the power from the dummy load, R_6 , to the non-inductively wound filament (R_4) in the calorimeter. The current during the vaporization time is measured as the voltage drop across the precision resistance (R_1) and through S_1 to the Brown instrument No.1. The voltage and during this



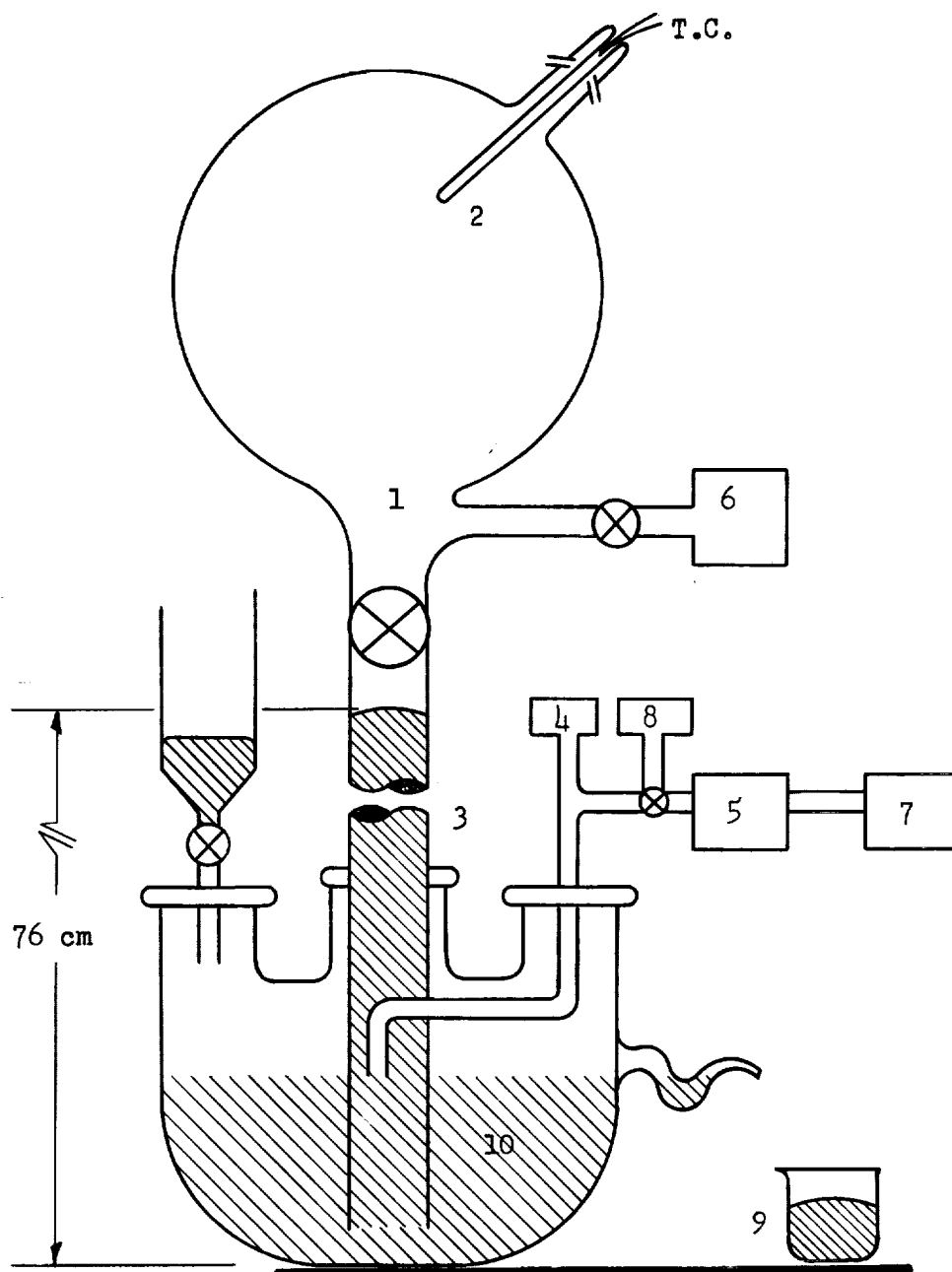
KEY

- R_1 .01 Ω
- R_2 100K
- R_3 2K
- R_4 WORK COIL, 10 Ω
- R_5 POWER CONTROL
- R_6 DUMMY LOAD, 10 Ω
- S_1, S_2 KNIFE SWITCHES
- S_3 TIMER SWITCH
- 1,2 BROWN HIGH SPEED RECORDERS
- 3 STANDARD VOLTAGE SOURCE

FIGURE 2 FILAMENT POWER SOURCE AND POWER MEASUREMENT

period is also measured as the voltage drop across a precision resistor (R_3) and plotted on another Brown instrument No. 2. The resistors R_1 , R_2 , and R_3 are all of the high precision type with known values to 1 part in 10^5 and kept at a constant temperature. Since the accuracy of the Brown instruments is not within the perscribed limit, after the current and voltage curves are produced the knife switches, S_1 and S_2 , will be thrown to a standard voltage source (3) which will be used to reproduce the existing curves. This would provide an accuracy of at least ± 0.01 millivolts since the reproducability of the Brown recorder is within this limit when a full scale span is one millivolt. Both Brown instruments are adapted for variable zero point (0 - 50 mv) and variable span (1 - 50 mv). On this basis the power input to the tungsten coil can be estimated to within 0.05% which is in the range of the desired accuracy.

During the fashing of the filament the heat carried to the calorimeter walls in the form of silver vapor and radiant energy will transform the liquid argon at its atmospheric pressure boiling point to gaseous argon at atmospheric pressure. The conversion value is about 14.5 cc of gas (STP) per calorie of heat evolved; and, since about 75 calories of heat are anticipated approximately one liter of gas will be evolved. The gas is to be measured in a gas burette of the type illustrated in Figure 3. Since the temperature of the gas as it leaves the calorimeter will be about -180°C , the gas will pass through an automatic heater (5) to raise the output stream temperature to at least 25°C . The pressure will in this line (5) is maintained at atmospheric pressure by raising or lowering the mercury column (3) with respect to the surface of the mercury bath (10). The pressure at this point is measured with an oil manometer (4).



KEY

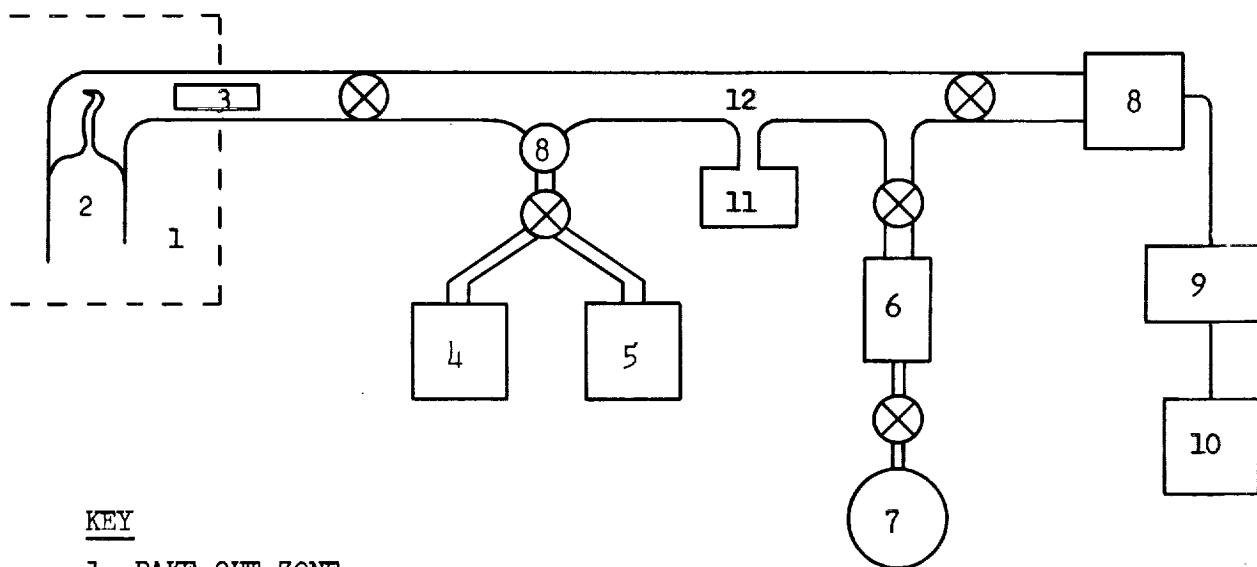
1. CALIBRATED VOLUME (3liters)
2. THERMOCOUPLE
3. MERCURY COLUMN
4. OIL MANOMETER
5. TEMPERATOR REGULATOR
6. VACUUM SYSTEM
7. CALORIMETER
8. HEAT LEAK STANDARD
9. COLUMN HEIGHT AS A FUNCTION OF MERCURY MASS
10. MERCURY BATH

FIGURE 3 GAS BURETTE

Prior to the flashing of the silver the calorimeter, heat leak rate is measured with a similar gas burette (8) with a smaller volume; and when this is established accurately the three way valve to isolate this system and to initiate the depicted system is manipulated. The time interval from this point is recorded such that the heat leak rate correction may be applied upon completion of the run.

Also prior to opening the three way line valve, a 10^{-5} Torr vacuum is placed above the column in the calibrated volume (1) from the side arm (6). This will raise a 76 cm column of mercury up the calibrated (gms Hg/mm column) column (3). Excess mercury to adjust the bath level (10) is supplied as illustrated. The argon gas from the calorimeter will pass up the mercury column into the calibrated volume, lower the mercury maniscus and force the bath (10) to overflow into (9) where it is collected for weighing. The change in mercury column length due to pressure change is measured as grams of Hg and compared to the calibration curve for a pressure measurement. The amount of gas at STP produced from the calorimeter is estimated from the published PVT data on argon and these data converted to calories produced in the calorimeter.

Upon completion of the energy measurements the Granville-Phillips valve (8), Figure 1, to isolate the UHV pumping and pressure measuring system will be closed to prevent adsorption of the CH_4 on the titanium getter cell. The BET apparatus shown in Figure 3 for surface area measurement will be brought into play by magnetically moving the iron slug (3) to smash the break-off tip (2). Prior to the opening of the BET system the pressure within the calibrated volume to the tip will be evacuated and flushed with CH_4 to a pressure of about 10^{-6} Torr at which point the vacuum system (8, 9, 10) is isolated. Thus,



KEY

1. BAKE-OUT ZONE
2. GLASS BREAK TIP
3. MAGNETIC BREAKER
4. LARGE VOLUME MCLEOD GAUGE
5. SMALL VOLUME MCLEOD GAUGE
6. GLASS CAPILLARY LEAK
7. CH₄ TANK
8. LIQUID NITROGEN TRAP
9. DIFFUSION PUMP
10. MECHANICAL PUMP
11. VACUUM GAUGE
12. CALIBRATED VOLUME

FIGURE 4 BET APPARATUS

the CH_4 at 10^{-6} Torr in a known volume will expand into the calorimeter of known volume and the pressure recorded. A second quantity of CH_4 will then be isolated in (12) through adjustment of the CH_4 leak (6), the pressure measured and the gas again allowed to expand into the calorimeter. Through this technique a BET adsorption isotherm can be obtained from which a value of the surface area may be obtained.

Progress Report

1. Calorimeter: The materials for the construction of this device are on hand and ready to be assembled. The construction has been delayed in ⁶leiv of the standardization of other components which is now underway.
2. Power Measuring Unit: A prototype has been constructed and used in the manner discussed. A study of techniques to attain the desired error in watts of about 0.02% consumed a considerable amount ⁸time.
3. Gas Burette: The materials for the construction are on hand and ready for standardization.
4. BET Apparatus: The BET system has been constructed and is currently undergoing standardization utilizing the power unit to flash silver pellets into a pyrex system at liquid nitrogen temperatures. Preliminary results suggest that a larger surface area than estimated will be attained.
5. Ultra High Vacuum System: In all probability a new system will be constructed since the two units currently available are in use (of Section I and Section III).

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PART III

DETERMINATION OF THE STRUCTURE OF THE
INTERFACE FORMED ADHESION

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THE DETERMINATION OF INTERMEDIATE PHASES PRESENT
IN THE INTERFACE BETWEEN A METALLIC THIN FILM AND
A METAL SUBSTRATE BY ELECTRON DIFFRACTION

Introduction

The ideal approach to the understanding of the crystal structure of an adhesion interface would be to construct such an interface by allowing atoms in a monolayer of the second metal to attain their equilibrium positions on the pure metal substrate; and then, determine these atomic positions. Successive layers would then be added until the bulk structure of the second metal was realized. If diffusion was restricted by maintaining a low temperature, a reasonable simulation of an adhesion weld could be reproduced. Current work by Germer et al (1-3) at Bell Laboratories with low energy electron diffraction (100 volts) seems to place this ideal approach well within experimental reach; however, before such an involved program is undertaken, a preliminary survey study of this area will be made. The preliminary problem will involve the deposition of a very thin film of nickel on an atomically clean substrate of aluminum at various temperatures and attempt to determine the metallurgical phases present by normal transmission electron diffraction techniques.

The apparatus to deposit the film consists of an ultra high vacuum cell (E) and system as described in Part I in which is placed a tungsten filament which heats a nickel rod (B) to its boiling point as shown in Fig. I. The nickel atom beam passes through a collimating shield (C) and deposits on aluminum plate (D) which was cleaned by argon ionic bombardment as described in Part I of this report. Due to the scatter within the atom beam the outer edges of the aluminum plate should be covered with an extremely thin layer of

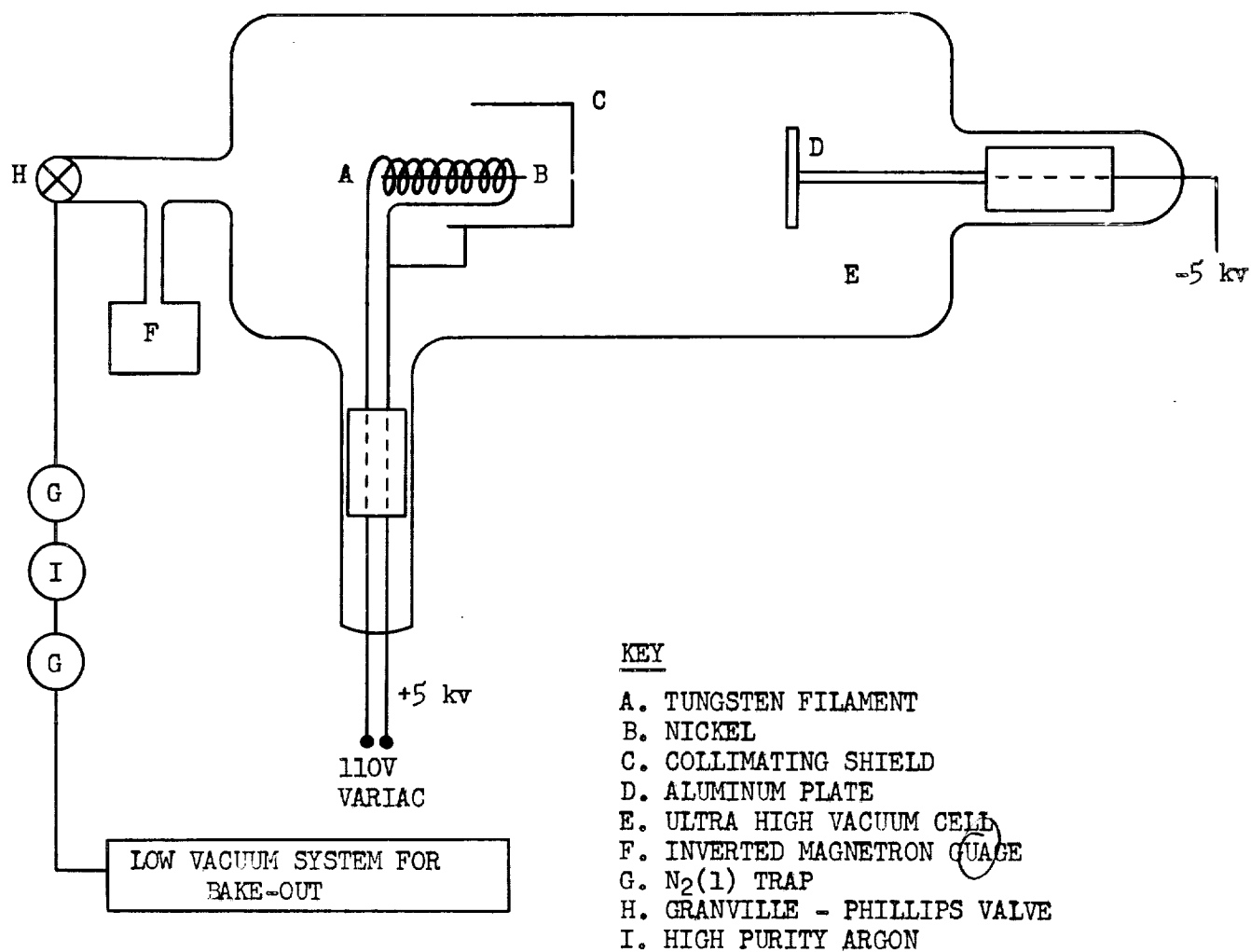


FIGURE 1 PREPARATION OF THIN METALLIC FILM ON ATOMICALLY CLEAN METAL SUBSTRATE

nickel atoms while the region at the center should be reasonably thick. An electron diffraction scan from the edges of the plate to the center should provide structural information at varying degrees of thickness of film.

Several specimens were prepared and mounted in a RCA - EMV - 3 electron microscope adapted for reflection diffraction. The only adaptor available for the diffraction operation was loaned to the University by RCA but not with a RCA recommendation since the apparatus was out of date. Several diffraction trials proved fruitless^f and, substantiated the lack of interest in the adaptor. Since the electron microscope unit can be used for transmission diffraction, this approach is the next to be considered. This technique is approximately the same as previously described, except that the aluminum plate before the deposition of nickel must be reduced in thickness to about 2000 Å. The 2000 Å thickness is sufficiently thin to allow an electron beam to pass through the specimen, to diffract and to excite a photographic plate.

The aluminum plate, .035", was annealed for two hours at 350°C and furnace cooled prior to exposure to the electroplating solution* recommended by Battelle Memorial Institute. The edges of the aluminum plate were coated with micro-stop to prevent desintegration. The center dissolved at a rate of about 0.001"/10 minutes. The details of the technique have been described by Thomas (4). Six plates have been prepared and are awaiting the deposition of the nickel layer, and subsequent electron diffraction analysis.

Preliminary X-Ray analysis of an aluminum layer on a nickel substrate indicated the presence of NiAl with trace amounts of NiAl_3 or Ni_2Al_3 . The NiAl is expected on the basis of free energy of formation data.

* Note: 45% H_3PO_4 , 41% H_2SO_4 , 14% H_2O ; 75°C; 3 v: stainless steel cathode

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